EXHIBIT 31

MULTIVARIABLE STUDY ON HOMOEPITAXIAL GROWTH OF DIAMOND ON
PLANAR AND NON-PLANAR SUBSTRATES

by

GOPI KRISHNA SAMUDRALA

YOGESH K. VOHRA, CHAIR
SHANE A. CATLEDGE
JOSEPH G. HARRISON
RAYMOND G. THOMPSON
UDAY K. VAIDYA

A DISSERTATION

Submitted to the graduate faculty of The University of Alabama at Birmingham,
in partial fulfillment of the requirements for the degree of
Doctor of Philosophy

BIRMINGHAM, ALABAMA

2009

UMI Number: 3389807

UMI®

Dissertation Publishing

ProQuest®

CHAPTER 4

DIAMOND GROWTH MECHANISM

4.1: Introduction

From the experiments conducted on planar, non-planar substrates, an understanding of changes in diamond growth rates, surface morphologies have been obtained. The systematic studies on CVD diamond growth described in previous chapters have important implications in understanding diamond growth mechanisms. To develop a full theory of diamond growth mechanism, complete understanding of the following areas is required. 1) Gas phase kinetics and plasma formation, which depend on the type of energy source that has been chosen, 2) Behavior of growth radicals in the plasma, their concentrations near substrate surface and finally 3) Dynamics of growth species on the substrate surface. Molecular dynamics simulations and density functional theory calculations combined with data from experimental observations can provide insight into each of the three areas.

As mentioned in Chapter 1, complete understanding of these areas has not yet been achieved. Also, since the growth conditions for nano diamond, microcrystalline diamond and single crystal diamond are different; it is not possible to come up with a unified theory for diamond growth. Any small variation in growth conditions can lead to huge changes in the behavior of growth radicals in the plasma and near the substrate surface and it is nearly impossible to account for all possible changes in a theoretical explanation. That said, a simplified explanation for diamond growth for a given set of

conditions can still be developed. An attempt has been made in this thesis to come up with such a simplified explanation for the diamond growth mechanism at the conditions which have been experimentally studied in previous chapters. Out of all the CVD techniques, combustion CVD of diamond has been the best understood owing to decades of research in which the possible reaction sets have been studied theoretically and at the same time comparing them experimentally. The gas phase chemistry and conduction of growth species is well understood in combustion CVD of diamond [37, 38, 39]. Such an attempt has been made in microwave CVD regime as well [40, 41, 42]. It is to be noted, however, that the growth conditions and gas phase mixtures based on which the simulations in previous works have been performed are different from those in this thesis research. Following is a brief summary of the simplified growth mechanism presented in the aforementioned works. It is to be noticed that the following explanation considers only hydrogen and methane as the gas phase precursors.

When the microwave energy couples with the gas phase precursors, they are dissociated into radicals with large number of electrons also being released. Microwaves then couple with the electrons and the energetic electrons further dissociate the gas phase precursors. The first reaction to take place is the dissociation of molecular hydrogen into atomic hydrogen.

$$H_2 \rightarrow 2H$$
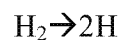
Although 99% of reactant mixture is atomic hydrogen, the dissociation of molecular hydrogen is only of the order of 40% to 60% depending on process conditions.

Below pressures of 1 atm, recombination of atomic hydrogen is slow and a super-equilibrium state of atomic hydrogen exists [43].

In the plasma a great number of reactions take place. Some examples are given below.

$$H+CH_4 \rightarrow CH_3+H_2$$

$$CH_3+CH_3+M \rightarrow C_2H_6+M$$

$$C_2H_X+H \rightarrow C_2H_{X-1}+H_2$$
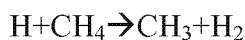
Once the growth radicals are transported near the surface, the reactions taking place at the surface of the substrate determine the uniformity and growth rate of the film.

On the substrate surface, adsorption, diffusion, reaction and desorption of various species occurs leading to the nucleation of diamond, suppression of graphitic (sp^2 bonded) carbon and ultimately growth of continuous diamond film. This is a complex process with many variations, and in which specific mechanisms occur. Since diamond is the metastable state with respect to graphite at the process conditions in MPCVD, the first phase encountered is graphite, not diamond. However, graphite will not spontaneously transform further into diamond because it is the stable phase and because of the high activation barrier between the two phases. Atomic hydrogen changes the relative energies of small graphitic and diamond nuclei and provides a means of circumventing the large activation barrier.

The substrate surface is assumed to be completely hydrogen terminated by this point. Creation of radical sites, adsorption of growth radicals onto the surface and desorption of byproducts are the next steps by which carbon atoms are incorporated into the diamond lattice. The following equations are some of the reactions that take place on

the substrate surface. "C_S" indicates a site on the substrate surface and "C_S^*" indicates a site where a radical can come and readily adsorb.

$$H+C_S \rightarrow C_S\text{-}H$$

$$C_S\text{-}H+H \rightarrow C_S^*+H_2$$

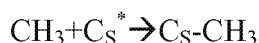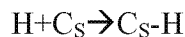$$CH_3+C_S^* \rightarrow C_S\text{-}CH_3$$

Figure 4.1 shows the various stages by which carbon atoms are adsorbed onto the substrate surface. For this example, only CH_3 has been chosen. However, radicals such as C_XH_Y also play an important role in extension of diamond lattice. Please refer to [42] for an in-depth discussion on the fate of various carbon growth radicals. When the gas phase precursors are dissociated, the substrate surface is covered by atomic hydrogen. Abstraction of these hydrogen atoms from the substrate surface paves the way for the growth radicals to adsorb onto the surface and therefore place the carbon atoms in the diamond lattice. Considering the case of CH_3, after the radical replaces the atomic hydrogen on the surface; the carbon has no covalent bonds left whereby another radical can come and attach itself. Then the following set of reactions take place to further incorporate the other radicals.

Hydrogen abstraction from adsorbed CH_3 radical takes place.

$$C_S\text{-}CH_3+H \rightarrow C_S\text{-}C^*H_2+H_2$$
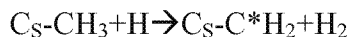
It is followed by attachment of another CH_3 radical in place of abstracted hydrogen atom.

$$C_S\text{-}C^*H_2+CH_3 \rightarrow C^*H_2\text{-}CH_3$$
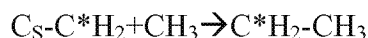
Removal of hydrogen from first CH_3 radical continues until all covalent bonds are formed with carbon atoms.

$$C^*H_2\text{-}CH_3+H \rightarrow C^*H\text{-}CH_3+H_2$$
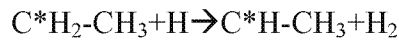
In the presence of other growth precursors such as nitrogen, which is believed to have a catalytic effect on diamond growth and oxygen, which has the property of preferentially etching the non- (100) diamond; the reactions that take place on the substrate surface are much more complex.

4.2: Qualitative study on diamond growth

The studies discussed so far have been effects of various parameters on diamond growth. Because the studies examined their effects individually, the insight obtained into diamond growth mechanism itself has been limited. Following will be the description of experiments conducted to study the coupling effect of these parameters and the results obtained. Another goal behind this qualitative study has been examining the possibility of growing thick single crystal samples. An important criterion for growing thick single crystal samples is to not have excessive twinning on the samples. Although some of the twinning can be polished away, twinning implies high nitrogen inclusion in the diamond film and it may not be useful for practical applications.
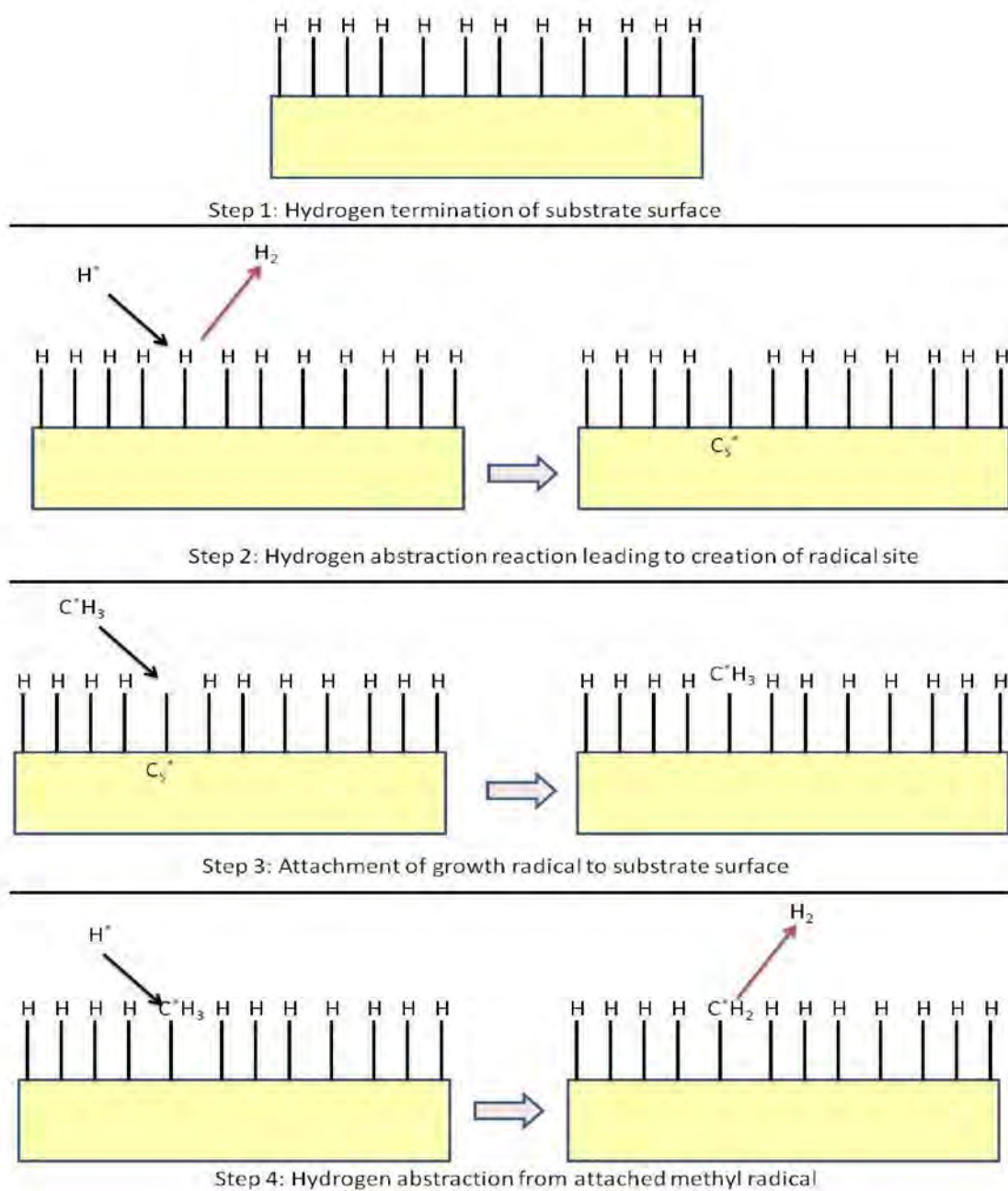
Figure 4.1: Illustration of the most basic reactions that take place on substrate surface during CVD of diamond.

The first parameter to be studied was oxygen. Oxygen is known to preferentially etch away non-(100) diamond. However, it also decreases the growth rate during CVD. Using both non-planar and planar substrates depositions were carried out without oxygen. For non-planar substrates, a standard gas phase mixture of 390 sccm of H_2, 0.4 sccm of N_2 and 8.0 sccm of CH_4 was used. The final film morphology revealed twinning on the surface indicating inclusion of high nitrogen content in the grown diamond film and at the same time, no significant improvement in growth rate has been observed. Since the resulting diamond film morphology is not suitable for designer diamond anvil work, oxygen has been made a standard component in the feed gas mixture for CVD on non-planar substrates. For planar substrates, a sample with feed gas mixture consisting of 390 sccm of H_2, 0.4 sccm of N_2 and 23.4 sccm of CH_4 has been prepared for comparison with sample 8 (Table 3.1). Whereas the sample prepared with oxygen in the plasma showed significantly less twinning on the surface, the sample prepared without oxygen showed lot of twinning and a comparison of the Photoluminescence signals reveal high nitrogen inclusion in the sample grown without oxygen. Again, oxygen has been made a standard component of the feed gas mixture for depositions on planar substrates. Figure 4.2 shows the optical microscopy images of samples grown with and without oxygen in feed gas mixture and the comparison of PL signals for planar substrates has also been included. Also diamond was grown on non-planar substrate with a feed gas mixture of 2% CH_4/H_2 and 1000 ppm of N_2 at a substrate temperature of 1050 C. In stark contrast to the observed result from planar substrates, no growth rate enhancement was obtained on non-planar substrate. In fact growth rate decreased when substrate temperature has been

decreased from 1200 C to 1050 C. This again confirms that homoepitaxial diamond growth is very much dependent on substrate geometry.

Since a chemistry for planar substrates has been found with which diamond film can be grown with relatively less nitrogen content and considerably less twinning on the surface when compared to other chemistries, the chemistry used to grow sample 8 (Table 3.1) – 6% CH_4/H_2, 1000 ppm N_2 and substrate temperature of 1200 C - has been chosen to grow thick single crystal sample. Whereas a growth rate of 42 microns/hr has been observed over a growth period of 3 hours, when a sample with the same chemistry has been grown for 10 hours, the growth rate fell to 28 microns/hr.

Because a temperature of 1050 C has been determined as optimum temperature for the chemistry 2% CH_4/H_2 and 1000 ppm of N_2; CVD deposition was carried out on three planar substrates for ten hours each with a feed gas mixture of 6% CH_4/H_2 and 1000 ppm N_2 at substrate temperatures of 1050 C, 110 C and 1200 C to observe the coupling effect of temperature and methane content. Remarkably, high methane content in the plasma has reversed the nitrogen incorporation trend observed in Figure 3.8. As the temperature increased from 1050 C to 1200 C, the nitrogen incorporation in the CVD diamond films decreased. It is accompanied by an increase in growth rate which again is in contrast to the results from Figure 3.7. As the substrate temperature increases from 1050 C to 1100 C and finally 1200 C; their respective growth rates were measured as 20 µm/hr, 22 µm/hr and 28 µm/hr. The inclusion of less nitrogen in the films as temperature increases manifests itself as decrease in twinning on the samples and the Photoluminescence data confirms this trend.
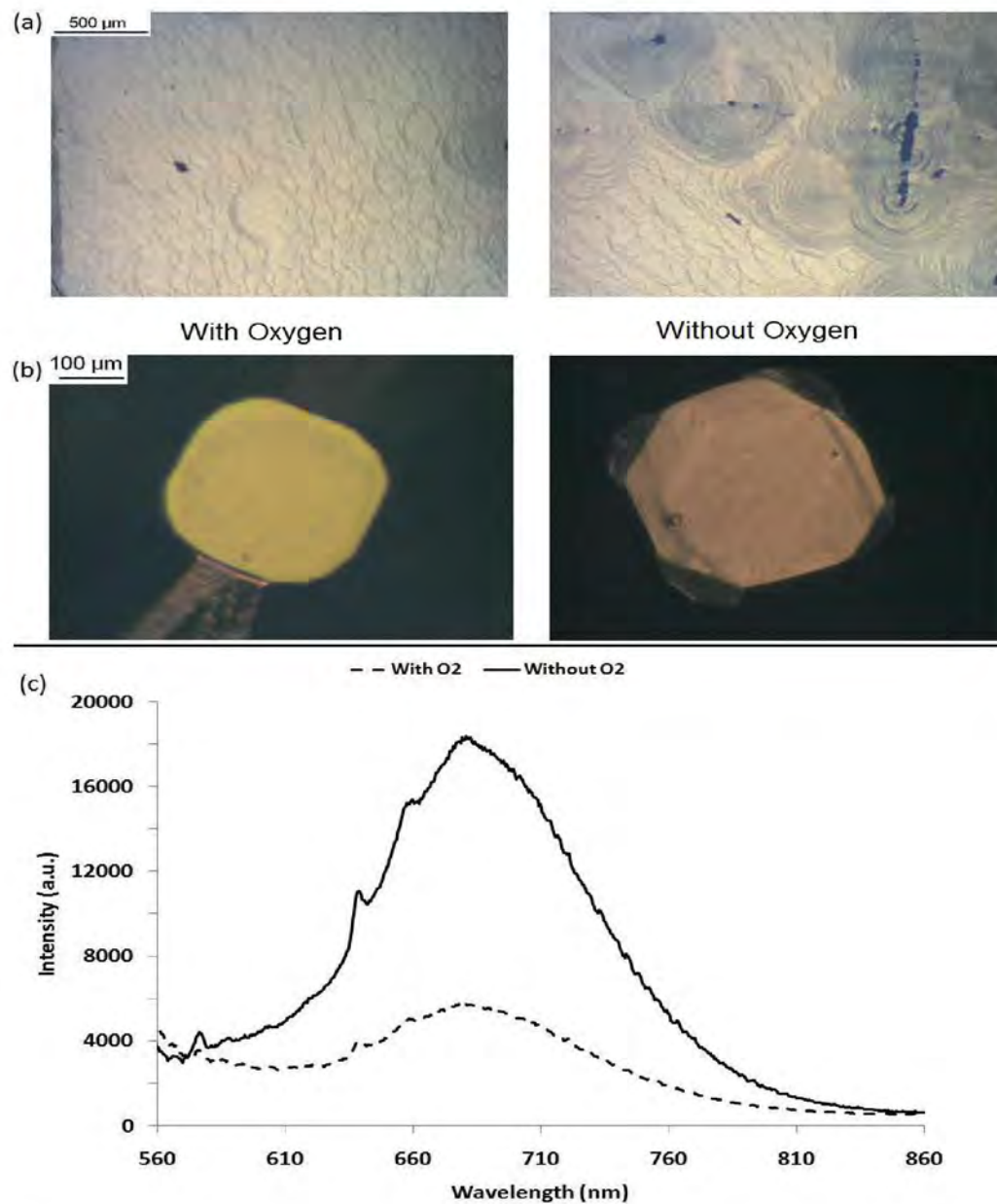
Figure 4.2: (a) Optical microscope images of CVD diamond films grown on planar substrates with and without oxygen.

(b) Optical microscope images of CVD diamond films grown on non planar substrates with and without oxygen.

(c) Photoluminescence spectra of films grown on planar substrates.

Once it has been established that 1200 C of substrate temperature is conducive for diamond growth when there is 6% CH_4/H_2 in the feed gas mixture, samples were prepared with 2500 ppm and 3000 ppm N_2 in the feed gas mixture. Both samples resulted in poor film morphology and these chemistries were also rendered unusable owing to excessive twinning on the surface. Another factor which renders all these chemistries unusable for long periods of growth is the polycrystalline diamond growth at the edges of the plates. Although this polycrystalline growth can be cut away by laser or polished away mechanically, great amount of carbon would then have been wasted in the growth process and in polishing. In Figure 4.3, the optical microscope images of the three samples prepared at different substrate temperatures are shown and their PL signals are compared.

Substrate holder geometry and the microwave power have prevented further addition of methane to the feed gas mixture. The holder geometry itself has been suspected as the reason for the polycrystalline diamond growth at the edges of these planar substrates. As the next step in this qualitative study, experiments were conducted with modified substrate holder geometry. Figure 4.4 shows the earlier version and modified version of the substrate holder. All experiments on planar substrates described up until this point have been conducted with the substrate holder design where only 0.5 mm of substrate has been exposed to the plasma. Discussion of the experiments conducted with new substrate holder and their results follow.
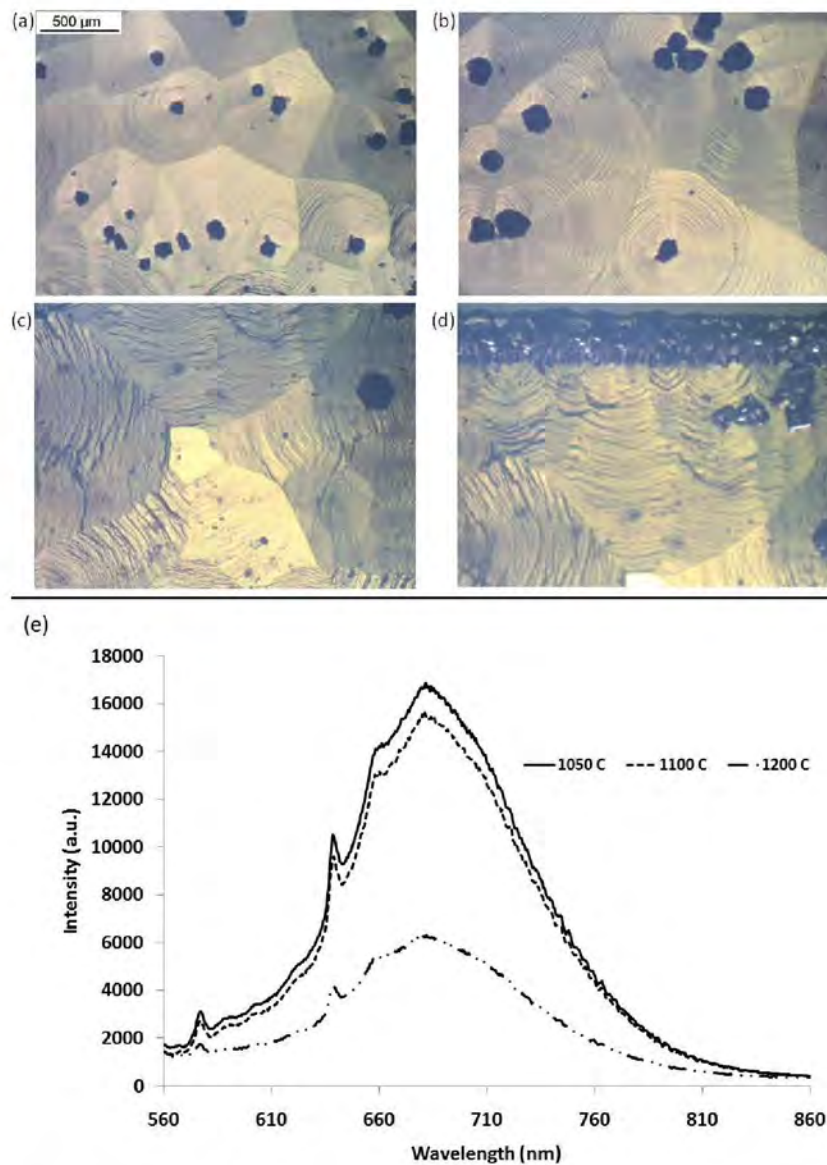
Figure 4.3: (a), (b) and (c) show the optical microscopy images of samples grown for 10 hours at 1050 C, 1100 C and 1200 C respectively.

(d) Shows the polycrystalline diamond growth at the edge of sample prepared at 1200 C.

(e) shows comparison PL signals for all three samples.
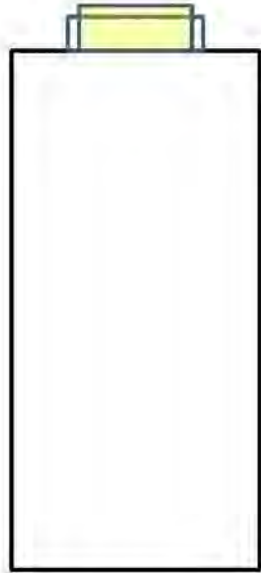
Substrate design 1 with only 0.5 mm of substrate exposed to the plasma
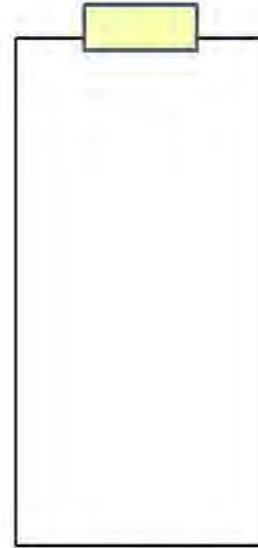
Substrate design 2 with 1.0 mm of substrate exposed to the plasma

Figure 4.4: Earlier version and modified versions of substrate holders.

A sample with the chemistry 6% CH_4/H_2 and 1000 ppm N_2 has been grown for 10 hours using the new substrate holder design where most of the substrate has been exposed to the plasma for comparing it with the sample prepared with same chemistry using old substrate holder design. No significant improvement in growth rate has been noticed between the two samples. However, the polycrystalline growth at the edges of the plates subsided considerably when the new substrate holder design has been used, but at the same time density of twins on the surface increased with the new substrate holder design.

Perhaps the most significant observation is that the new substrate design allowed for addition of more methane to the feed gas mixture. Diamond films were grown with 7% CH_4/H_2 in the feed gas mixture at substrate temperature of 1100 C and 1200 C. Temperature of 1200 C could not be sustained for long periods owing to the 1200 W limit on microwave power. A thick single crystal diamond of 0.6 mm was grown with 7% CH_4/H_2; 1000 ppm N_2 at 1100 C after CVD was carried out for 30 hours. When this chemistry was used for CVD, the twinning on the surface vanished and the polycrystalline growth on the edges subsided considerably. Using 8% CH_4/H_2 and 1000 ppm N_2 two diamond samples were grown for twenty hours each at temperatures of 1050 C and 1100 C respectively. Figure 4.5 shows the surfaces of various samples described above.

From the qualitative study conducted on planar substrates, it has been observed that for growing thick single crystal samples; a feed gas mixture of 8% CH_4/H_2 and 1000 ppm N_2 is ideal with the substrate design where most of the substrate is exposed to the plasma.

6% CH_4/H_2 1000 ppm N_2
1200 C (new holder design)

6% CH_4/H_2 1000 ppm N_2
1200 C (old holder design)

7% CH_4/H_2 1000 ppm N_2
1100 C (new holder design)

8% CH_4/H_2 1000 ppm N_2
1100 C (new holder design)

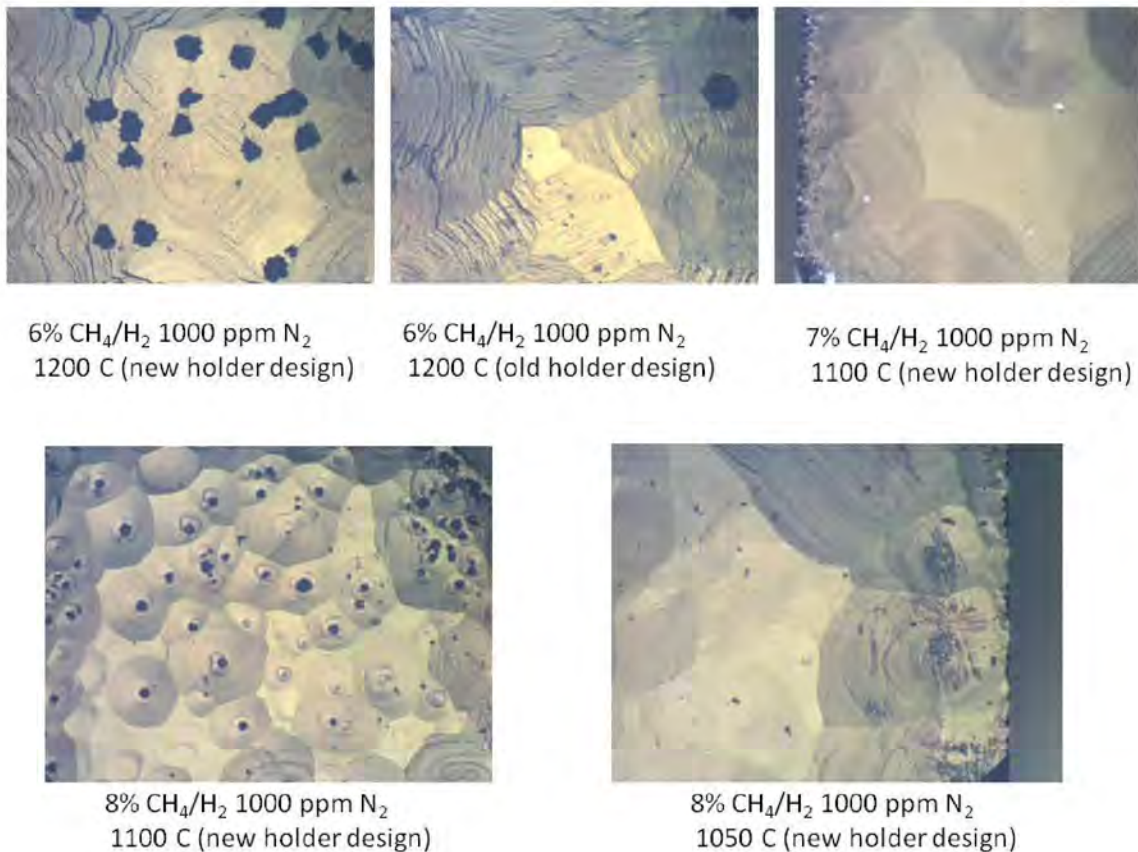8% CH_4/H_2 1000 ppm N_2
1050 C (new holder design)

Figure 4.5: Optical microscopy images of different diamond films grown on planar substrates with high methane content.

There are areas which have not been investigated concerning diamond growth on planar substrates. For example, it has been found that growth rate is higher at higher temperature when 6% CH_4/H_2 was used. Such an observation was not possible when 7% CH_4/H_2 and 8% CH_4/H_2 were used because of the limitation on microwave power. Similarly coupling effect of nitrogen and temperature was not studied at high methane content.

4.3: Discussion on diamond growth mechanism

As described in section 4.1, the first step in diamond growth from vapor phase is hydrogenation of substrate surface. In an ideal situation, all the hydrogen atoms in a given plane are abstracted by the methyl radicals and other hydrocarbons forming a perfect plane of carbon containing radicals. Then, hydrogen atoms from these hydrocarbons would be further abstracted by other hydrocarbon radicals forming the basis of a perfect diamond lattice. This does not always happen. To begin with, the defect centers on the substrate surface prevent formation of perfect plane of carbon atoms on which a diamond lattice could be constructed. Also to be noticed is the fact that hydrocarbons other than methyl radicals such as acetylene radicals participate in hydrogen abstraction reaction. Sometimes, grouping of such carbons atoms with double bonds prevents extension of diamond lattice from that point leading to interstitial defects.

In growth processes where feed gases other than hydrogen and source of carbon are used (such as this thesis research); the reactions taking place on the surface are more complex. The entire growth process of diamond from vapor phase is based on three very important types of reactions on the substrate surface viz. abstraction of atomic hydrogen from the surface, diffusion of hydrocarbons on the substrate surface and finally desorption of growth radicals from the substrate surface back into the plasma environment. Presence of nitrogen and oxygen greatly alter the reaction rates and as a result the growth rate and surface morphology are affected. Another important parameter which has a great influence on the diamond growth is the substrate temperature. It has a direct impact on the residence time of growth radicals on the surface as well as their

desorption rate from the surface. At optimum temperature, there is a delicate balance between the flow of the growth radicals to the surface and desorption of growth radicals from the surface. Below substrate temperatures of 900 C, the adsorption of species is in the form of physisorption and above 900 C; the adsorption of species is in the form of chemisorptions [44]. This is why diamond growth cannot be explained based on role played by one parameter alone. Coupling effects of all parameters involved in the experiment need to be taken into consideration to explain the growth process.

In the studies conducted in order to understand the role of nitrogen and temperature in diamond growth [44-50]; it was found that in the plasma phase the production of CN and HCN has a direct dependence on the amount of CH_4 being added in the feed gas mixture. The reactive nature of nitrogen species such as NH_X, CN and HCN is strongly dependent on substrate temperature. Inclusion of nitrogen in diamond lattice has direct impact on subsequent abstractions reactions.

To correlate these findings with the experimental results observed, a summary of results is necessary.

Growth conditions	N_2 incorporation trend in CVD diamond
2% CH_4/H_2 Substrate temp of 1200 C	N_2 incorporation increases with increased addition of N_2 to feed gas mixture
6% CH_4/H_2 Substrate temp of 1200 C	N_2 incorporation increases with increased addition of N_2 to feed gas mixture
2% CH_4/H_2 1000 ppm N_2	N_2 incorporation increases with increase in substrate temperature
6% CH_4/H_2 1000 ppm N_2	N_2 incorporation decreases with increase in substrate temperature

Table 4.1: Summary of nitrogen incorporation trends observed

The following conclusions can be reached from the observations summarized above. When high amount of nitrogen is present in the feed gas mixture, the nitrogen containing compounds such as HCN, CN and NH_X are active at substrate temperature of 1200 C and incorporate aggressively into the diamond lattice regardless of concentration of hydrocarbons on the surface. The reason could be that at 1200 C, the nitrogen compounds gain enough energy to overcome the activation energy needed for them to be incorporated into the diamond lattice. High nitrogen incorporation in CVD diamond does not always translate to high growth rates. In determining an optimum temperature for diamond growth, the methane concentration and nitrogen concentration need to have a fine balance. The optimum temperature shifts higher as the C/N ratio increases. To achieve low incorporation of nitrogen in the CVD diamond films, it is necessary to have high C/N ratio in the feed gas mixture and at the same time the substrate temperature should be high enough to provide energy for hydrocarbons to adsorb into the diamond lattice.